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(54) Title: POLYMERIC MATERIALS

(57) Abstract

An oligomer or polymer of the formula (I): $Q^1 - X^1 - Y^1 - Z - W$ wherein Q^1- represents a hydrophobic moiety, $-X^1-$ and $-Y^1-$ are independently each absent or represent a suitable linking group, $-Z-$ represents a hydrophilic chain; and $-W$ represents hydrogen or a group of the formula $-Y^2-X^2-Q^2$, each of $-X^2$, $-Y^2$ and $-Q^2$ being independently selected from the values for X^1, Y^1 and Q^1 as hereinbefore defined.

POLYMERIC MATERIALS

FIELD OF THE INVENTION

5 The present invention is concerned with polymeric materials
which are useful for endowing desirable rheological
properties to a particular class of aqueous liquid
detergent compositions. This class of aqueous compositions
comprises those which contain sufficient detergent-active
10 material and, optionally, sufficiently dissolved
electrolyte to result in a structure of lamellar droplets
dispersed in a continuous aqueous phase.

BACKGROUND OF THE INVENTION

15

Lamellar droplets are a particular class of surfactant
structures which, _inter_ _alia_, are already known from a
variety of references, e.g. H.A. Barnes, 'Detergents', Ch.2
in K.Walters (Ed), Rheometry: Industrial Applications', J.
20 Wiley & Sons, Letchworth 1980.

Such lamellar dispersions are used to endow properties such
as consumer-preferred flow behaviour and/or turbid
appearance. Many are also capable of suspending
25 particulate solids such as detergency builders or abrasive
particles. Examples of such structured liquids without
suspended solids are given in US patent 4 2444 840, whilst
examples where solid particles are suspended are disclosed
in specifications EP-A-160 342: EP-A-38 101: EP-A-104 452
30 and also in the aforementioned US 4 244 840. Others are
disclosed in European Patent Specification EP-A-151 884,
where the lamellar droplets are called 'spherulites'.

The presence of lamellar droplets in a liquid detergent
product may be detected by means known to those skilled in
the art, for example optical techniques, various
5 rheometrical measurements, X-ray or neutron diffraction,
and electron microscopy.

The droplets consist of an onion-like configuration of
concentric bi-layers of surfactant molecules, between which
10 is trapped water or electrolyte solution (aqueous phase).
Systems in which such droplets are close-packed provide a
very desirable combination of physical stability and solid-
suspending properties with useful flow properties.

15 The viscosity and stability of the product depend on the
volume fraction of the liquid which is occupied by the
droplets. Generally speaking, the higher the volume
fraction of the dispersed lamellar phase (droplets), the
better the stability. However, higher volume fractions
20 also lead to increased viscosity which in the limit can
result in an unpourable product. This results in
compromise being reached. When the volume fraction is
around 0.6 or higher, the droplets are just touching
(space-filling). This allows reasonable stability with an
25 acceptable viscosity (say no more than 2.5 Pas, preferably
no more than 1 Pas at a shear rate of $21s^{-1}$). This volume
fraction also endows useful solid-suspending properties.

A complicating factor in the relationship between stability
30 and viscosity on the one hand and, on the other, the volume
fraction of the lamellar droplets, is the degree of
flocculation of the droplets. When flocculation occurs

between the lamellar droplets at a given volume fraction, the viscosity of the corresponding product will increase owing to the formation of a network throughout the liquid. Flocculation may also lead to instability because

5 deformation of the lamellar droplets, owing to flocculation, will make their packing more efficient. Consequently, more lamellar droplets will be required for stabilisation by the space-filling mechanism, which will again lead to a further increase of the viscosity.

10

The volume fraction of droplets is increased by increasing the surfactant concentration whereas flocculation between the lamellar droplets occurs when a certain threshold value of the electrolyte concentration is crossed at a given

15 level of surfactant (and fixed ratio between any different surfactant components). Thus, in practice, the effects referred to above mean that there is a limit to the amounts of surfactant and electrolyte which can be incorporated whilst still having acceptable product properties. In

20 principle, higher surfactant levels are required for increased detergency (cleaning performance). Increased electrolyte levels can also be used for better detergency, or are sometimes sought for secondary benefits such as building.

25

According to the specification of EP-A-346 995, the dependency of stability and/or viscosity upon volume fraction is favourably influenced by incorporating into the lamellar dispersion, a deflocculating polymer comprising a

30 hydrophilic backbone and one or more hydrophobic side-chains.

4

The theory of function of these deflocculating polymers is
that the hydrophobic chains are anchored in the outer
bilayer of the lamellar droplet. The hydrophilic part is
extended outwards. These hydrophilic 'brushes' are
5 responsible for the steric stabilisation of the droplets,
provided that the 'brushes' exceed a certain length. For
surfactant blends in common use, the optimum length of the
polymer hydrophobic chain, in order to be anchored into the
bilayer is in the order of C_{12} - C_{15}, about the length of
10 the surfactants in the droplet. However, for reducing
viscosity, the number of hydrophobic anchors per polymer
molecule should be limited to one, otherwise one polymer
chain could link two droplets which results in gelling of
the dispersion due to bridging.

15

EP-A-438 215 discloses preparation of acrylic acid telomers
with a functional terminal group, using a secondary alcohol
chain transfer agent which may, for example be a C_6 - C_{12}
monofunctional secondary alcohol. These materials are
20 described as detergent additives, in particular
sequestrants or anti-precipitants. The materials are
produced using polymerisation initiators such as ditertiary
butyl peroxide. In the description of various different
possible initiators, there is mentioned lauryl peroxide.
25 However, there is no example described of use of lauryl
peroxide to produce a C_{12} hydrophobe - terminated
polyacrylate. Moreover, the telomers are not disclosed as
having any efficacy in controlling the rheological
properties of lamellar droplet-structured aqueous detergent
30 liquids and indeed, aqueous detergent liquids are not
mentioned at all.

Some specific kinds of deflocculating polymers which
contain only one hydrophobic moiety and which is attached
to an end position of a hydrophilic chain, are disclosed in
EP-A-623 670.

5

Various sub-types are described for the deflocculating
polymers in EP-A-623 670. However, many of those actually
exemplified are thiol polyacrylates, that is to say,
materials formed by polymerisation of acrylic acid in the
10 presence of a hydrophobic chain transfer agent having from
five to twenty five carbon atoms and a terminal-SH group,
in a radical polymerisation process. Analagous materials
having a thia linkage between the hydrophilic and
hydrophobic parts of the molecule are disclosed in US-A-5
15 489 395, US-A-5 489 397 and EP-A-691 399.

It is also now believed that the molecular weight of the
deflocculating polymer should exceed a certain value in
order to avoid 'building in' of the whole polymer inside
20 the droplets. The applicants have discovered that the
optimum molecular weight seems to be about 2500, a
compromise of deflocculating efficiency and cost
efficiency.

25 Typical examples of the polymer disclosed in EP-A-346 995
are made by a radical copolymerization of acrylic acid and
laurylmethacrylate. This results in a random distribution
of lauryl chains over the polymer. As a consequence, most
of the polymer molecules have one hydrophobic chain per
30 molecule. However, a reasonable fraction of the polymer
molecules have more than one hydrophobic anchors per

6

molecule. The last fraction may give rise to a viscosity
increase due to bridging.

The polymers as disclosed in EP-A-623 679, EP-A-691 399 and
5 US-A-5 489 397 being 'end-capped', in principle have a
lower fraction of polymer molecules with more than one
hydrophobic anchor as compared with the polymers described
in EP-A-346 995. However, the described synthesis routes
of these end-capped polymers are rather limited and produce
10 polymers which are not optimal in their performance. A new
class of polymers constituted by the first aspect of the
present invention overcomes, according to the particular
new polymer in question, one or more of these drawbacks.

15 <u>SUMMARY OF THE INVENTION</u>

Thus, the present invention now provides an oligomer or
polymer of formula (I)
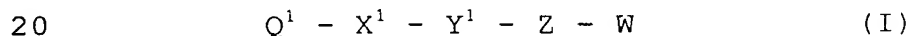
20          $Q^1 - X^1 - Y^1 - Z - W$ (I)

wherein Q^1- represents a hydrophobic moiety, $-X^1-$ and $-Y^1-$
are independently each absent or represent a suitable
linking group, $-Z-$ represents a hydrophilic chain; and
25 $-W$ represents hydrogen or a group of formula $-Y^2-X^2-Q^2$, each
of $-X^2,-Y^2$ and $-Q^2$ being independently selected from the
values for X^1, Y^1 and Q^1 as hereinbefore defined.

<u>DETAILED DESCRIPTION OF THE INVENTION</u>
30

<u>Oligomer or Polymer</u>

7

Preferably Q^1 represents an optionally substituted $C_5 - C_{30}$
alkyl, C_5-C_{30} alkenyl or C_5-C_{30} aralkyl group, or a
hydrophobic monomer residue, such as from lauryl
methacrylate or a hydrophobically modified TEMPO (2,2,6,6-
5   tetramethylpiperdinyl-1-oxy) moiety. Alkyl, alkenyl or
aralkyl groups most preferably have from 8 to 18 carbon
atoms and are preferably straight-chained or have only
limited branching. Preferably, X^1 is absent or represents
a group of formula $(-CH_2-)_n$ where n is 1 or 2 or X^1 is
10 phenyl. Preferably, Y^1 is absent or represents a carbonyl
group, an ester linkage, a hydroxy C_{1-5} alkyl group or a
silyl group of formula $(-SiR^1R^2)$, where R^1 and R^2
independently represent $-CH_3$ or $-C_2H_5$; or else Y^1 is a thia-,
aza-, carboxy- (i.e. ester), carboxy-aza-, phosphoryl-,
15 phosphonyl- or phosphinyl- linkage, but then with the
proviso that W is not hydrogen.

The group -Z- is preferably a linear, branched or slightly
crosslinked molecular composition containing one or more
20 types of relatively hydrophilic monomer units. Preferably
the hydrophilic monomers themselves are sufficiently water
soluble to form at least a 1% by weight solution when
dissolved in water. The only limitations to the structure
of -Z- are that the resultant polymer of formula (I) must
25 be suitable for incorporation in an active-structured
aqueous liquid detergent composition and that a polymer
corresponding to the hydrophilic moiety alone, i.e. H-Z-H
is relatively soluble in water, in that the solubility in
water at ambient temperature and at a pH of 3.0 to 12.5 is
30 preferably more than 1 g/l, more preferred more than 5 g/l,
most preferred more than 10 g/l.

8

Preferably the group -Z- is predominantly linear; more
preferably the main chain of the backbone constitutes at
least 50% by weight, preferably more than 75%, most
preferred more than 90% by weight of the backbone.

5

The group -Z- is generally composed of monomer units, which
can be selected from a variety of units available for the
preparation of polymers.

10 Examples of types of monomer units for inclusion alone or
in combination in -Z- are:
(i)   Unsaturated C_1-C_6 acids, ethers, alcohols, aldehydes,
ketones or esters. Preferably these monomer units are
mono-unsaturated. Examples of suitable monomers are
15 acrylic acid, methacrylic acid, maleic acid, crotonic acid,
itaconic acid, aconitic acid, citraconic acid, vinyl-methyl
ether, vinyl sulphonate, vinylalcohol obtained by the
hydrolysis of vinyl acetate, acrolein, alkenyl alcohol and
vinyl acetic acid. The corresponding salts, e.g. alkali
20 metal salts such as the sodium salt, are also included.

(ii) Cyclic units, either being unsaturated or comprising
other groups capable of forming inter-monomer linkages. In
linking these monomers the ring-structure of the monomers
25 may either be kept intact, or the ring structure may be
disrupted to form the backbone structure. Examples of
cyclic monomer units are sugar units, for instance
saccharides and glucosides; alkoxy units such as ethylene
oxide and hydroxy propylene oxide; and maleic anhydride.
30

(iii)   Other units, for example glycerol, polyalkylene
oxide(s) or unsaturated polyalcohol(s) .

Each of the above mentioned monomer units for inclusion in
-Z- may be substituted with groups such as amino, ammonium,
amide, sulphonate, sulphate, phosphonate, phosphate,
5 hydroxy, carboxyl and oxide groups.

The group -Z- is preferably composed of one or two monomer
types but also possible is the use of three or more
different monomer types in one hydrophilic backbone.
10 Examples of preferred hydrophilic backbones are:
homopolymers of acrylic acid, copolymers of acrylic acid
and maleic acid, poly (2-hydroxy ethyl acrylate),
polysaccharides, cellulose ethers, polyglycerols,
polyacrylamides, polyvinylalcohol/polyvinylether
15 copolymers, poly sodium vinyl sulphonate, poly 2-sulphato
ethyl methacrylate, polyacrylamido methyl propane
sulphonate and copolymers of acrylic acid and trimethylol
propane triacrylate.

20 Optionally, the group -Z- may also contain small amounts of
relatively hydrophobic units, e.g. those derived from
polymers having a solubility of less than 1g/l in water,
provided that the overall solubility of the hydrophilic
polymer backbone still satisfies the solubility
25 requirements as specified hereabove. Examples of
relatively water insoluble polymers are polyvinyl acetate,
polymethyl methacrylate, polyethyl acrylate, polyethylene,
polypropylene, polystyrene, polybutylene oxide,
polypropylene oxide and polyhydroxy propyl acetate.
30

Preferred sub-classes of the oligomers or polymers of
formula (I) (hereinafter referred to as "materials of the

10

invention"), include respectively, those where W is hydrogen, those where W is $-Y^2-X^2-Q^2$, some or all of X^2, Y^2 and Q^2 respectively differing from X^1, Y^1 and Q^1 and those where W is $-Y^2-X^2-Q^2$, X^2, Y^2 and Q^2 each being the same as
5 X^1, Y^1 and Q^1.

If W is hydrogen, there is only a single hydrophobic moiety attached to one end of the hydrophilic moiety. Such materials are ideally suited as deflocculating materials.
10 If W is a group $-Y^2-X^2-Q^2$ then there is a respective hydrophobic group at either end of the hydrophobic moiety. Such materials may be employed for deliberate bridging of lamellar droplets, e.g. to increase viscosity.

15 Of course, as mentioned above, often deflocculation is needed to inhibit viscosity increase at high volume fractions so that in principle, bridging can be undesirable. However, the bridging materials having a pair of hydrophobic groups (W not hydrogen) are within the ambit
20 of the present invention. For example, a predetermined blend of materials of the invention may be used, comprising one deflocculating material to control stability and one bridging material to increase viscosity in a controlled fashion.
25

The bridging material has, on average, more than one hydrophobic (Q^1/Q^2) groups per molecule and preferably two or more such hydrophobic groups. As a consequence the molecular weight (Mw) of the bridging material is larger
30 than (x.Mi + Mo), preferably larger than (x.Mi + 2Mo) and more preferably larger than 2(x.Mi + Mo), with x being the molecular ratio between hydrophilic monomers and

hydrophobic monomers, Mi being the average molecular weight
of the hydrophilic groups and Mo the average molecular
weight of the hydrophobic groups.

5 The bridging polymer is preferably prepared using
conventional aqueous polymerisation procedures, but
employing a process wherein the polymerisation is carried
out in the presence of a suitable cosolvent and wherein the
ratio of water to cosolvent is carefully monitored so as to
10 keep the polymer as it forms in a sufficiently mobile
condition and to prevent unwanted homopolymerisation and
precipitation of the polymer from the hydrophobic monomer.
The process of the invention provides a product which is
stable and clear and which exhibits no gelling or product
15 separation on standing. Suitable cosolvents are selected
from the group consisting of isopropanol, n-propanol,
acetone, lower (C_1 to C_4) alcohols, esters and ketones and
wherein the water to cosolvent ratio is smaller than 1.5,
more preferably less than 1.0, more preferably less than
20 0.75, and especially less than 0.5.

The use of a better defined mixture of a deflocculating
material and of a bridging material allows a degree of
control of rheology not possible with the "cocktail" of
25 polymers resulting from the process of EP-A-346 995.

Nevertheless, it should be appreciated that any method of
forming either the deflocculating (W=H) or bridging (W= –
Y^2-X^2-Q^2) oligomers or polymers of formula (I) will not form
30 100% pure materials. However, sample oligomers or polymers
according to the present invention will have a high weight
percentage of oligomer or polymer species having a

structure of formula (I), although not necessarily all of
that percentage will have the same structure of formula
(I). Thus, a preferred sample or batch of oligomer and/or
polymer material the present invention may have at least
5 50% by weight of its total of oligomers and/or polymers
having the general formula (I) as defined in claim 1, or
optionally, of any preferred sub-class of polymers or
oligomers of formula (I) as defined in the description or
any other claim. This weight percentage is more
10 preferably, in ascending order of preference, at least 65%,
70%, 75%, 80%, 85% or 90% by weight of the total batch or
sample.

Materials of the present invention preferably have a
15 molecular weight of at least 500, more preferably at least
1000, still more preferably at least 2000 . Also, their
molecular weight is preferably no more than 50,000, more
preferably no more than 30,000 and especially, no more than
10,000, less than 5,000.
20

Any reference herein to determination of oligomer or
polymer molecular weight refers to the number-averaged
degree of polymerisation as determined using ^{1}H-NMR
spectroscopy by comparing the intensities of the NMR peaks
25 corresponding to the terminal methyl group (from the
initiator) at ca. 0.95 ppm and the polymer backbone
$-CH_2-$ and $-CH-$ at 2.2 ppm, respectively. This so-called
determination of end groups is a well-known procedure, cf.
J.C. Bevington, J.R. Ebdon, and T.N. Huckerby, in *NMR*
30 *Spectroscopy of Polymers*, R.N. Ibbett (Ed.), Chapman &
Hall, Glasgow: 1993, and R.G. Garmon in *Polymer Molecular*

Weights, Part I, P.E. Slade, Jr. (Ed.), Marcel Dekker, New
York: 1975.

The aforementioned method demands high accuracy of the
5 integration of the NMR spectra, which is especially
important if the degree of polymerisation exceeds ca. 100.
To check its accuracy a high-molecular weight poly(acrylic
acid) was synthesised using 1 mol% of AIBN, in the absence
of transfer agent. The molecular weight of this polymer
10 was determined using both the end group (NMR) method and
viscosimetry. The intrinsic viscosity of the polymer was
determined to be 0.193 ± 0.008 dl/g. From this value, the
viscosity-averaged molecular weight (M_v) was calculated to
be 51500 (cf. S. Newman, W.R. Krigbaum, C. Laugier, and
15 P.J. Flory, *J. Polym. Sci* 1954, *14* 451). From NMR, the
number-averaged molecular weight (M_n) was found to be ca.
25000. It is known from the literature H.F. Mark, N.H.
Biktales, C.G. Overberger, G. Menger and J.I. Kroschwitz
(Eds), 'Encyclopedia of Polymer Science and Engineering',
20 p. 280; 2nd ed. Vol. 3; Wiley, New York 1985 that for
polydisperse samples $M_n < M_v < M_w$. Since M_w/M_n could be as high
as 5-10 for unfractionated poly(acrylic acid) samples at
high conversion, the determined ratio of $M_v/M_n = 2$ is
therefore reliable.
25

Preparation of the Oligomer or Polymer

Preferred methods of preparing materials of the invention
will vary according to the kind of material required.
30 Thus, a second aspect of the present invention provides a
method of preparing an oligomer or polymer of formula (I)

as hereinbefore defined, by reacting a compound of formula (IV)

$$Q^1-X^1-Y^1-Y^2 \qquad (IV)$$

5

wherein Q^1 X^1 and Y^1 are as hereinbefore defined and Y^2 is a reactive hydrogen or a free radical, with a precursor material, in the presence of an initiator.

10 The term "reactive hydrogen" is herein defined as referring to a bond heat of formation between 96 and 80 kcal/mol, preferably between 92 and 85 kcal/mol (as mentioned in 'Handbook of Chemistry and Physics', pages F223-F229, 56 ed. 1975-1976) (such as a TEMPO deriviative). The
15 precursor material is a monomer or prepolymer, containing at least one polymerizable group, said monomer or polymer being capable of forming a group of formula $-Z-W$ as hereinbefore defined.

20 The compound of formula (IV) may for example be a compound wherein X^1 is absent, Y^1 represents a carbonyl group or $-COH(R^5)-$ wherein R^5 is a C_{1-4} alkyl group; and if W is not hydrogen, then Y^1 can be a thia group.

25 Alternatively, an oligomer or polymer of formula (I) may be prepared by reacting a compound of formula (V)

$$Q^1 - G - Q^1 \qquad (V)$$

30 wherein Q^1 is as hereinbefore defined with a precursor material as hereinbefore defined and Q^1-G-Q^1 is a molecule capable of cleavage to form a radical of formula $-Q^1-X^1-Y^1$.

15

In the compound of formula (V), G may for example be -CO-O-O-CO- or -N=N- and the precursor material may comprise a radical-forming compound and one or more monomers for
5 forming the group -Z-.

A radical initiator containing the hydrophobic group Q^1 is a compound which can initiate chemical reactions by producing free radicals as mentioned in Kirk-Othmer,
10 "Encyclopaedia of Chemical Technology, 4th edition, volume 14, page 431-460. A suitable example of such a radical initiator is dilauroyl peroxide (Q = undecyl). Other examples: diisononanoyl peroxide (Q = iso-octyl), dicumylperoxide (Q = 1-cyano-cyclohex-1-yl).
15

Control of both hydrophobic endgroups (Q^1, Q^2) can also be achieved by, for example, a so-called living polymerisation. A possible procedure involves a controlled radical polymerisation, involving TEMPO (2,2,6,6-
20 tetramethylpiperidinyl-1-oxy) and a normal, e.g. peroxide radical initiator, as described in J.Am.Chem.Soc. 1994, 116, 11185-11186, by Craig J. Hawker.

Typically in a first step one starts with a compound of
25 formula (IV), TEMPO and initiator. The product obtained from this reaction is then used in a second step by heating it in the presence of a precursor as hereinbefore defined giving a polymer with a hydrophilic backbone having on the one end a hydrophobic group and on the other the
30 thermolabile TEMPO group. Heating this polymer in the presence of a hydrophobic monomer (e.g. laurylmethacrylate)

inserts the monomer resulting in a copolymer with two
hydrophobic endgroups.

In another embodiment one could use a hydrophobically
5 modified TEMPO molecule obviating the last insertion step.
In still another embodiment one starts with a mix of
TEMPO, initiator and a hydrophobic monomer giving a
hydrophobic starting block which can be further elaborated
as above.
10

In yet another embodiment, one could use a compound of
formula (V) as initiator in combination with TEMPO as
described above, for giving a copolymer with two
hydrophobic endgroups.
15

Detergent Compositions

A further aspect of the present invention provides an
aqueous liquid detergent composition in the form of a
20 dispersion of lamellar droplets, the composition comprising
water, surfactant, a material of the invention and
optionally electrolyte. Such compositions are hereinafter
referred to as compositions according to the present
invention. Materials of the invention can be incorporated
25 in such aqueous detergent lamellar dispersions to provide
stable, pourable products preferably wherein the volume
fraction of the lamellar phase is 0.5-0.6 or higher.

Lamellar Droplet Phase
30

The volume fraction of the lamellar droplet phase may be
determined by the following method. The composition is

centrifuged, say at 40,000 G for 12 hours, to separate the composition into a clear (continuous aqueous) layer, a turbid active-rich (lamellar) layer and (if solids are suspended) a solid particle layer. The conductivities of
5 the continuous aqueous phase, the lamellar phase and of the total composition before centrifugation are measured. From these, the volume fraction of the lamellar phase is calculated, using the Bruggeman equation, as disclosed in American Physics, 24, 636 (1935). When applying the
10 equation, the conductivity of the total composition must be corrected for the conductivity inhibition owing to any suspended solids present. The degree of correction necessary can be determined by measuring the conductivity of a model system. This has the formulation of the total
15 composition but without any surfactant. The difference in conductivity of the model system, when continuously stirred (to disperse the solids) and at rest (so the solids settle), indicates the effect of suspended solids in the real composition. Alternatively, the real composition may
20 be subjected to mild centrifugation (say 2,000 G for 1 hour) to just remove the solids. The conductivity of the upper layer is that of the suspending base (aqueous continuous phase with dispersed lamellar phase, minus solids).
25

It should be noted that, if the centrifugation at 40,000 G fails to yield a separate continuous phase, the conductivity of the aforementioned model system at rest can serve as the conductivity of the continuous aqueous phase.
30 For the conductivity of the lamellar phase, a value of 0.8 $mS.cm^{-1}$ can be used, which is typical for most systems. In

18

any event, the contribution of this term in the equation is often negligible.

Preferably, the viscosity of the aqueous continuous phase
5 is less than 25 mPas, most preferably less than 15 mPas, especially less than 10 mPas, these viscosities being measured using a capillary viscometer, for example an Ostwald viscometer.

10 Sometimes, it is preferred for the compositions of the present invention to have solid-suspending properties (i.e. capable of suspending solid particles). Therefore, in many preferred examples, suspended solids are present. However, sometimes it may also be preferred that the compositions of
15 the present invention do not have solid suspending properties, this is also illustrated in the examples.

In practical terms, i.e. as determining product properties, the term 'deflocculating' in respect of the polymer means
20 that the equivalent composition, minus the polymer, has a significantly higher viscosity and/or becomes unstable. Although within the ambit of the present invention, relatively high levels of the deflocculating polymers can be used in those systems where a viscosity reduction is
25 brought about; typically levels as low as from about 0.01% by weight to about 1.0% by weight can be capable of reducing the viscosity at 21 s^{-1} by up to 2 orders of magnitude.

30 Especially preferred embodiments of the present invention exhibit less phase separation on storage and have a lower

viscosity than an equivalent composition without any of the
deflocculating polymer.

It is conventional in patent specifications relating to
5 aqueous structured liquid detergents to define the
stability of the composition in terms of the volume
separation observed during storage for a predetermined
period at a fixed temperature. In fact, this can be an
over-simplistic definition of what is observed in practice.
10 Thus, it is appropriate here to give a more detailed
description.

For lamellar droplet dispersions, where the volume fraction
of the lamellar phase is below 0.6 and the droplets are
15 flocculated, instability is inevitable and is observed as a
gross phase separation occurring in a relatively short
time. When the volume fraction is below 0.6 but the
droplets are not flocculated, the composition may be stable
or unstable. When it is unstable, a phase separation
20 occurs at a slower rate than in the flocculated case and
the degree of phase separation is less.

When the volume fraction of the lamellar phase is below
0.6, whether the droplets are flocculated or not, it is
25 possible to define stability in the conventional manner.
In the context of the present invention, stability for
these systems can be defined in terms of the maximum
separation compatible with most manufacturing and retail
requirements. That is, the 'stable' compositions will
30 yield no more than 2% by volume phase separation as
evidenced by appearance of 2 or more separate layers when
stored at 25°C for 21 days from the time of preparation.

In the case of the compositions where the lamellar phase volume fraction is 0.6 or greater, it is not always easy to apply this definition. In the case of the present invention, such systems may be stable or unstable,

5 according to whether or not the droplets are flocculated. For those that are unstable, i.e. flocculated, the degree of phase separation may be relatively small, e.g. as for the unstable non-flocculated systems with the lower volume fraction. However, in this case the phase separation will

10 often not manifest itself by the appearance of a distinct layer of continuous phase but will appear distributed as 'cracks' throughout the product. The onset of these cracks appearing and the volume of the material they contain are almost impossible to measure to a very high degree of

15 accuracy. However, those skilled in the art will be able to ascertain instability because the presence of a distributed separate phase greater than 2% by volume of the total composition will readily be visually identifiable by such persons. Thus, in formal terms, the above-mentioned

20 definition of 'stable' is also applicable in these situations, but disregarding the requirement for the phase separation to appear as separate layers.

Especially preferred embodiments of compositions according

25 to the present invention yield less than 0.1% by volume visible phase separation after storage at 25°C for 90 days from the time of preparation.

It must also be realised that there can be some difficulty

30 in determining the viscosity of an unstable liquid.

When the volume fraction of the lamellar phase is less than
0.6 and the system is deflocculated or when the volume
fraction is 0.6 or greater and the system is flocculated,
then phase separation occurs relatively slowly and
5 meaningful viscosity measurement can usually be determined
quite readily. For all compositions of the present
invention it is usually preferred that their viscosity is
not greater than 2.5 Pas, most preferably no more than 1.0
Pas, and especially not greater than 750 mPas at a shear
10 rate of $21s^{-1}$.

When the volume fraction of the lamellar phase is less than
0.6 and the droplets are flocculated, then often the rapid
phase separation occurring makes a precise determination of
15 viscosity rather difficult. However, it is usually
possible to obtain a figure which, whilst appropriate, is
still sufficient to indicate the effect of the
deflocculating polymer in the compositions according to the
present invention.
20

Generally, the amount of material of oligomer and/or
polymer of the present invention in any aqueous detergent
lamellar dispersion will be from 0.01% to 5.0% by weight in
the composition, most preferably from 0.1% to 2.0%.
25

Although it is possible to form lamellar dispersions of
surfactant in water alone, in many cases it is preferred
for the aqueous continuous phase to contain dissolved
electrolyte. As used herein, the term electrolyte means
30 any ionic water-soluble material. However, in lamellar
dispersions, not all the electrolyte is necessarily
dissolved but may be suspended as particles of solid

because the total electrolyte concentration of the liquid
is higher than the solubility limit of the electrolyte.
Mixtures of electrolytes also may be used, with one or more
of the electrolytes being in the dissolved aqueous phase
5   and one or more being substantially only in the suspended
solid phase.   Two or more electrolytes may also be
distributed approximately proportionally, between these two
phases.   In part, this may depend on processing, e.g. the
order of addition of components.   On the other hand, the
10 terms 'salts' includes all organic and inorganic materials
which may be included, other than surfactants and water,
whether or not they are ionic, and this term encompasses
the sub-set of the electrolytes (water-soluble materials).

15 The only restriction on the total amount of detergent-
active material and electrolyte (if any) is that in the
compositions of the invention, together they must result in
formation of an aqueous lamellar dispersion.   Thus, within
the ambit of the present invention, a very wide variation
20 in surfactant types and levels is possible.   The selection
of surfactant types and their proportions, in order to
obtain a stable liquid with the required structure will be
fully within the capability of those skilled in the art.

25 Detergent Active Material

However, it can be mentioned that an important sub-class of
useful compositions is those where the detergent-active
material comprises blends of different surfactant types.
30 Typical blends useful for fabric washing compositions
include those where the primary surfactant(s) comprise

nonionic and/or non-alkoxylated anionic and/or alkoxylated anionic surfactant.

In many (but not all) cases, the total detergent-active
5 material may be present at from 2% to 60% by weight of the total composition, for example from 5% to 40% and typically from 10% to 30% by weight. However, one preferred class of compositions comprises at least 15%, most preferably at least 25% and especially at least 30% of detergent-active
10 material based on the weight of the total composition. In the case of blends of surfactants, the precise proportions of each component which will result in such stability and viscosity will depend on the type(s) and amount(s) of the electrolytes, as is the case with conventional structured
15 liquids.

In the widest definition the detergent-active material in general, may comprise one or more surfactants, and may be selected from anionic, cationic, nonionic, zwitterionic and
20 amphoteric species, and (provided mutually compatible) mixtures thereof. For example, they may be chosen from any of the classes, sub-classes and specific materials described in 'Surface Active Agents' Vol. 1, by Schwartz & Perry, Interscience 1949 and 'Surface Active Agents' vol.
25 II by Schwartz, Perry & Berch (Interscience 1958), in the current edition of "McCutcheon's Emulsifiers & Detergents" published by the McCutcheon division of Manufacturing Confectioners Company or in 'Tensid-Taschenbuch", H. Stache, 2nd Edn,., Carl Hanser Verlag, München & Wien,
30 1981.

24

Suitable nonionic surfactants include, in particular, the
reaction products of compounds having a hydrophobic group
and reactive hydrogen atom, for example aliphatic alcohols,
acids, amides or alkyl phenols with alkylene oxides,
5 especially ethylene oxide, either alone or with propylene
oxide. Specific nonionic detergent compounds are alkyl
(C_6-C_{18}) primary or secondary linear or branched alcohols
with ethylene oxide, and products made by condensation of
ethylene oxide with the reaction products of propylene
10 oxide and ethylenediamine. Other so-called nonionic
detergent compounds include long chain tertiary amine
oxides, long-chain tertiary phosphine oxides and dialkyl
sulphoxides.

15 Suitable anionic surfactants are usually water-soluble
alkali metal salts of organic sulphates and sulphonates
having alkyl radicals containing from about 8 to 22 carbon
atoms, the term alkyl being used to include the alkyl
portion of higher acyl radicals. Examples of suitable
20 synthetic anionic detergent compounds are sodium and
potassium alkyl sulphates, especially those obtained by
sulphating higher (C_8-C_{18}) alcohols produced, for example,
from tallow or coconut oil, sodium and potassium alkyl (C_9-
C_{20}) benzene sulphonates, particularly sodium linear
25 secondary alkyl (C_{10}-C_{15}) benzene sulphonates; sodium alkyl
glyceryl ether sulphates, especially those ethers of the
higher alcohols derived from tallow or coconut oil and
synthetic alcohols derived from petroleum; sodium coconut
oil fatty monoglyceride sulphates and sulphonates; sodium
30 and potassium salts of sulphuric acid esters of higher (C_6-
C_{18}) fatty alcohol-alkylene oxide, particularly ethylene
oxide, reaction products; the reaction products of fatty

acids such as coconut fatty acids esterified with
isethionic acid and neutralised with sodium hydroxide;
sodium and potassium salts of fatty acid amides of methyl
taurine; alkane monosulphonates such as those derived by
5 reacting alpha-olefins (C_{8-20}) with sodium bisulphite and
those derived from reacting paraffins with SO_2 and Cl_2 and
then hydrolyzing with a base to produce a random
sulphonate; and olefin sulphonates, which term is used to
describe the material made by reacting olefins,
10 particularly C_{10}-C_{20} alpha-olefins, with SO_3 and then
neutralising and hydrolyzing the reaction product. The
preferred anionic detergent compounds are sodium (C_{11}-C_{15})
alkyl benzene sulphonates and sodium (C_{16}-C_{18}) alkyl
sulphates.

15

Also possible is that part or all of the detergent active
material is a stabilising surfactant, which has an average
alkyl chain length greater then 6 C-atoms, and which has a
salting out resistance, greater than, or equal to 6.4.
20 These stabilising surfactants are disclosed in EP-A-328
177. Examples of these materials are alkyl polyalkoxylated
phosphates, alkyl polyalkoxylated sulphosuccinates; dialkyl
diphenyloxide disulphonates; alkyl polysaccharides and
mixtures thereof.

25

It is also possible, and sometimes preferred, to include an
alkali metal soap of a long chain mono- or dicarboxylic
acid for example one having from 12 to 18 carbon atoms.
Typical acids of this kind are oleic acid, ricinoleic acid
30 and fatty acids derived from castor oil, rapeseed oil,
groundnut oil, coconut oil, palm kernel oil or mixtures

thereof.   The sodium or potassium soaps of these acids can
be used.

Water

5

Preferably the amount of water in the composition is from 5
to 95%, more preferred from 25 to 75%, most preferred from
30 to 50%. Especially preferred less than 45% by weight.

10 Electrolyte

The compositions optionally also contain electrolyte in an
amount .sufficient to bring about structuring of the
detergent-active material. Preferably though, the
15 compositions contain from 1% to 60%, especially from 10 to
45% of a salting-out electrolyte. Salting-out electrolyte
has the meaning ascribed to in specification EP-A-79 646.
Optionally, some salting-in electrolyte (as defined in the
latter specification) may also be included, provided if of
20 a kind and in an amount compatible with the other
components and the composition is still in accordance with
the definition of the invention claimed herein. Some or
all of the electrolyte (whether salting-in or salting-out),
or any substantially water-insoluble salt which may be
25 present, may have detergency builder properties. In any
event, it is preferred that compositions according to the
present invention include detergency builder material, some
or all of which may be electrolyte. The builder material
is any capable of reducing the level of free calcium ions
30 in the wash liquor and will preferably provide the
composition with other beneficial properties such as the
generation of an alkaline pH, the suspension of soil

removed from the fabric and the dispersion of the fabric softening clay material.

Detergency Builder

5

Examples of phosphorous-containing inorganic detergency builders, when present, include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates, polyphosphates and phosphonates. Specific examples of
10 inorganic phosphate builders include sodium and potassium tripolyphosphates, phosphates and hexametaphosphates. Phosphonate sequestrant builders may also be used.

Examples of non-phosphorous-containing inorganic detergency
15 builders, when present, include water-soluble alkali metal carbonates, bicarbonates, silicates and crystalline and amorphous aluminosilicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates and
20 zeolites.

In the context of inorganic builders, we prefer to include electrolytes which promote the solubility of other electrolytes, for example use of potassium salts to promote
25 the solubility of sodium salts. Thereby, the amount of dissolved electrolyte can be increased considerably (crystal dissolution) as described in UK patent specification GB 1 302 543.

30 Examples of organic detergency builders, when present, include the alkaline metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates,

polyacetyl carboxylates, carboxymethyloxysuccinates,
carboxymethyloxymalonates, ethylene diamine-N,N-disuccinic
acid salts, polyepoxysuccinates, oxydiacetates, triethylene
tetramine hexa-acetic acid salts, N-alkyl imino diacetates
5 or dipropionates, alpha sulpho- fatty acid salts,
dipicolinic acid salts, oxidised polysaccharides,
polyhydroxysulphonates and mixtures thereof.

Specific examples include sodium, potassium, lithium,
10 ammonium and substituted ammonium salts of ethylenediamino-
tetraacetic acid, nitrilo-triacetic acid, oxydisuccinic
acid, melitic acid, benzene polycarboxylic acids and citric
acid, tartrate mono succinate and tartrate di succinate.

15 In the context of organic builders, it is also desirable to
incorporate polymers which are only partly dissolved in the
aqueous continuous phase. This allows a viscosity
reduction (owing to the polymer which is dissolved whilst
incorporating a sufficiently high amount to achieve a
20 secondary benefit, especially building, because the part
which is not dissolved does not bring about the instability
that would occur if substantially all were dissolved).

Other Polymers

25

Examples of partly dissolved polymers include many of the
polymer and co-polymer salts already known as detergency
builders. For example, may be used (including building and
non-building polymers) polyethylene glycols, polyacrylates,
30 polymaleates, polysugars, polysugarsulphonates and co-
polymers of any of these. Preferably, the partly dissolved
polymer comprises a co-polymer which includes an alkali

metal salt of a polyacrylic, polymethacrylic or maleic acid
or anhydride.. Preferably, compositions with these co-
polymers have a pH of above 8.0 In general, the amount of
viscosity-reducing polymer can vary widely according to the
5 formulation of the rest of the composition. However,
typical amounts are from 0.5 to 4.5% by weight.

It is further possible to include in the compositions of
the present invention, alternatively, or in addition to the
10 partly dissolved polymer, yet another polymer which is
substantially totally soluble in the aqueous phase and has
an electrolyte resistance of more than 5 grams sodium
nitrilotriacetate in 100 ml of a 5% by weight aqueous
solution of the polymer, said second polymer also having a
15 vapour pressure in 20% aqueous solution, equal or less than
the vapour pressure of a reference 2% by weight or greater
aqueous solution of polyethylene glycol having an average
molecular weight of 6,000; said second polymer having a
molecular weight of at least 1,000.
20

The incorporation of the soluble polymer permits
formulation with improved stability at the same viscosity
(relative to the composition without the soluble polymer)
or lower viscosity with the same stability. The soluble
25 polymer can also reduce viscosity drift, even when it also
brings about a viscosity reduction. Here, improved
stability and lower viscosity mean over and above any such
effects brought about by the deflocculating polymer.

30 It is especially preferred to incorporate the soluble
polymer with a partly dissolved polymer which has a large
insoluble component. That is because although the building

capacity of the partly dissolved polymer will be good
(since relatively high quantities can be stably
incorporated), the viscosity reduction will not be optimum
(since little will be dissolved). Thus, the soluble
5 polymer can usefully function to reduce the viscosity
further, to an ideal level.

The soluble polymer can, for example, be incorporated at
from 0.05 to 20% by weight, although usually from 0.1 to
10 10% by weight of the total composition is sufficient, and
especially from 0.2 to 3.5 - 4.5% by weight. It has been
found that the presence of deflocculating polymer increase
the tolerance for higher levels of soluble polymer without
stability problems. A large number of different polymers
15 may be used as such a soluble polymer, provided the
electrolyte resistance and vapour pressure requirements are
met. The former is measured as the amount of sodium
nitrolotriacetate (NaNTA) solution necessary to reach the
cloud point of 100 ml of a 5% w/w solution of the polymer
20 in water at 25°C, with the system adjusted to neutral pH,
i.e. about 7. This is preferably effected using sodium
hydroxide. Most preferably, the electrolyte resistance is
10 g NaNTA, especially 15g. The latter indicates a vapour
pressure low enough to have sufficient water binding
25 capability, as generally explained in the applicants'
specification GB-A-2 053 249. Preferably, the measurement
is effected with a reference solution at 10% by weight
aqueous concentration, especially 18%.

30 Typical classes of polymers which may be used as the
soluble polymer, provided they meet the above requirements,

include polyethylene glycols, Dextran, Dextran sulphonates, polyacrylates and polyacrylate/maleic acid co-polymers.

The soluble polymer must have an average molecular weight
5 of at least 1,000 but a minimum average molecular weight of 2,000 is preferred.

The use of partly soluble and the use of soluble polymers as referred to above in detergent compositions is described
10 in our European patent specifications EP-A-301 882 and EP-A-301 883.

Hydrotrope

15 Although it is possible to incorporate minor amounts of hydrotropes such as lower alcohols (e.g. ethanol) or alkanolamines (e.g. triethanolamine), in order to ensure integrity of the lamellar dispersion we prefer that the compositions of the present invention are substantially
20 free from hydrotropes. By hydrotrope is meant any water soluble agent which tends to enhance the solubility of surfactants in aqueous solution.

Other Optional Ingredients
25

Apart from the ingredients already mentioned, a number of optional ingredients may also be present, for example lather booster such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and
30 coconut fatty acids, fabric softeners such as clays, amines and amine oxides; lather depressants, oxygen-releasing bleaching agents such as sodium perborate and sodium

32

percarbonate; peracid bleach precursors, chlorine-releasing
bleaching agents such as trichloroisocyanuric acid,
inorganic salts such as sodium sulphate, and, usually
present in very minor amounts, fluorescent agents,
5 perfumes, enzymes such as proteases, amylases, lipases
(including Lipolase (Trade Mark) ex Novo) and cellulases,
germicides and colourants, oily-soil release polymers, such
as Poly Ethylene Terephthalate - Poly Oxy Ethylene
Terephtalates or (partly) sulphonate versions thereof
10 (including Permalose and Aquaperle (Trademarks) ex. ICI,
Gerol and Repe-O-Tex (Trademarks) ex. Rhone-Poulenc and
Sokalan HP22 (Trademark) ex. BASF); anti-redeposition
agents, such as sodium carboxy methyl cellulose; anti-dye
transfer agents, such as PVP, PVI and co-polymers thereof.
15

Amongst these optional ingredients, as mentioned
previously, are agents to which lamellar dispersions
without deflocculating polymer are highly stability-
sensitive and by virtue of the present invention, can be
20 incorporated in higher, more useful amounts. These agents
cause a problem in the absence of deflocculating polymer
because they tend to promote flocculation of the lamellar
droplets. Examples of such agents are soluble polymers,
soluble builders such as succinate builders, fluorescers
25 like Blankophor RKH, Tinopal LMS, and Tinopal DMS-X and
Blankophor BBH as well as metal chelating agents,
especially of the phosphonate type, for example the Dequest
range sold by Monsanto.

30

EXAMPLES

The invention will now be illustrated by way of the
following Examples, in all Examples, unless stated to the
5 contrary, all percentages are by weight.

**Example 1:   Synthesis of mono-endcapped hydrophobically-
modified poly(sodium acrylate) using a hydrophobic
initiator in dioxane: solution polymerisation**

10

Materials:

monomer   : acrylic acid (AA), 5g (69.4 mmol), freshly-
             distilled (Janssen, 99%)

initiator : dilauroylperoxide (DLP), 0.57 g (1.43 mmol)
15   (Aldrich)

solvent   : dioxane, 50 ml (Merck, pro analysi)

Synthesis:

A 250 ml round-bottomed flask was loaded with 5 g of
20 acrylic acid, 50 ml of dioxane and 0.57g of
dilaurolylperoxide. The flask was connected to a reflux
condenser fitted with a $CaCl_2$-tube and was heated on an oil
bath at 80°C with stirring. The reaction mixture was kept
at this temperature overnight. After cooling to room
25 temperature, the clear, slightly viscous solution was
precipitated in 300 ml of pentane to remove most of the
dioxane. The viscous precipitate was dissolved in dry
methanol. The methanolic solution was slowly precipitated
in a stirred solution of 3.6 g (66.7 mmol) of sodium
30 methoxide in 100 ml of dry methanol. The white solid was
filtered off under reduced pressure. The crude product was
dried in vacuo at 30°C to remove most of the remaining

dioxane and methanol. The polymer was dissolved in water
to obtain a solution of about 5-10% (w/w). The polymer was
completely neutralised by adding sodium hydroxide until the
pH was 9, and the solution was freeze-dried. In order to
5 remove the last traces of solvent, the polymer was finely
powdered and dried at 60°C over P_2O_5 in vacuo for at least
2 hours.

Characterisation:
10 The absence of monomer was established by ^{1}H-NMR using the
characteristic peaks for the acrylic hydrogens at ca. 6
ppm. We note the importance of pH in recording the NMR
spectra. At pH 1 the peaks are broader and shifted upfield
relative to a solution of pH 10. This is due to a
15 conformational change of the polymer from a compact globule
at low pH to a more extended coil at high pH (cf. J. Jager,
Ph. D. Thesis, Groningen, 1987). All NMR spectral data
presented correspond to pH 10.

20 MALDI-TOFSPEC was employed to unambiguously demonstrate
that the polymer molecules mainly contain only one
hydrophobic chain.

The characteristics of the polymer were as follows:
25   - Degree of polymerisation (DP) = 97; MW = 9200 (see
            addendum 1)
          - Efficiency of initiation = 25%
The product is essentially an unidecyl or a dodecyl chain
connected to (on average) 97 sodium acrylate moieties, i.e.
30 in structural terms according to formula I: $Q^1 = C_{11}H_{23}-$; Y^1
= -COO- or absent ; X^1 is absent; Z = $(CH_2-C(H)(COON_a))_{97}-$;
W=H.

Example 2:   Synthesis of mono-endcapped hydrophobically-
modified poly(sodium acrylate) using a hydrophobic
initiator in 2-butanone (MEK): precipitation
5 **polymerisation.**

Materials:
monomer   : acrylic acid (AA), 5 g (69.4 mmol), freshly-
            distilled
10 initiator : dilauroylperoxide (DLP), 1.14 g (2.86 mmol)
   solvent   : 2-butanone (MEK), 50 ml (Merck, pro analysi)

The synthesis, purification and characterisation of the
polymer were analogous to those employed in Example 1 with
15 the following exceptions.

During the reaction in MEK, a glassy precipitate was formed
which is the desired polymer. The polymerisation was
complete after 5 hours. After reaction, the mixture was
20 cooled to room temperature, the solvent was decanted and
the solid was dissolved in methanol. In principle, the MEK
could be re-used. The methanolic solution containing the
poly(acrylic acid) was precipitated in pentane, and worked-
up as described above.
25

The characteristics of the polymer were as follows:
       - DP = 123; MW = 11700 (see addendum 2)
       - Efficiency of initiation = 10%
The structure of the polymer according to formula I reads:
30 $Q^1=C_{11}H_{23}-$; $Y^1=-COO-$or absent; X^1 is absent; $Z=-(CH_2-$
$C(CH)(COON_a))_{123}-$; W is H.

●   ●

Example 3:   **Synthesis of mono-endcapped hydrophobically-modified poly(sodium acrylate) using 2-tetradecanol as a hydrophobic transfer agent in 2-butanone (MEK): precipitation polymerisation.**

5

Materials:

monomer   : acrylic acid (AA), 5 g (69.4 mmol), freshly-
               distilled

initiator : azo-bis-isobutyronitril (AIBN), 0.14 g (0.85
10   mmol)

transfer agent : 2-tetradecanol, 7.49 g (34.9 mmol)

solvent   : 2-butanone (MEK), 50 ml, pro analysi

Synthesis:

15 The same procedure was followed as described for Example 2.
However, instead of n-dodecyl-mercaptane, 2-tetradecanol
was used. This alcohol was synthesised from 1-
bromododecane and distilled acetaldehyde according to a
literature procedure (Pickard, R.H.; Kenyon, J. *Ind Eng.*
20 *Chem.* 1940, *32,* 206).

Characterisation:

In order to prove that the hydrophobic modification was not
due to esterification of the alcohol with the acrylic acid,
25 the polymer was treated with aqueous sodium hydroxide (pH
12) for 1 week. This treatment did not affect the NMR
spectral characteristics of the polymer during this time,
which provides evidence that no hydrolysis had taken place.
Therefore, the alcohol is probably connected to the
30 poly(acrylate) moiety through a C-O bond, which is most
likely due to incorporation of the secundary alcohol by a
radical transfer mechanism.

37

The characteristics of the polymer were as follows:
     - DP = 112; MW = 10600
The chemical structure of the polymer reads, according to
5 formula I:
$Q^1 = C_{12}H_{25}-$; $Y^1 = -C(CH_3)(OH)-$; $X^1 =$ absent; $Z = -(CH_2-$
$C(H)(COON_a))_{112}-$; W is H.

**Example 4 Synthesis of double-endcapped poly(sodium
10 acrylate)s for deliberate bridging**

The double-endcapped (α,ω)-bis-dodecylthiapoly(acrylate)
used as said agent for deliberate bridging of lamellar
droplets can be prepared by polymerising acrylic acid in
15 the presence of a radical initiator, and alkylsulfides as
chain transfer agents. The degree of polymerisation (DP)
of the resulting polymer can be predicted according to the
Mayo equation: $1/DP = 1/DP_0 + C_{tr}*[CTA]/[AA]$
where DP_0 is the degree of polymerisation in the absence of
20 chain transfer agent, C_{tr} is the chain transfer constant
($C_{tr} = 2*10^{-4}$ for didodecylsulfide), [CTA] is the molar
concentration of the chain transfer agent, and [AA] is the
molar concentration of acrylic acid. DP_0 can easily exceed
the value of 1000 for acrylic polymers, and so this term
25 can be neglected here, where the desired degree of
polymerisation is 40-100.

These considerations lead to the following proposed
procedure. To obtain the abovementioned desired polymer
30 having a degree of polymerisation between 40 and 100 (ca.
4000 < MW < ca. 10000), acrylic acid is dissolved in liquid
didodecyl sulfide at 60-80°C in 0.16-0.43% by weight,

respectively. AIBN (2,2'-Azobisisobutyronitrile) is added
in 0.23% by weight with respect to acrylic acid to initiate
the polymerisation. The mixture is heated at 60-80°C for
three hours. When the reaction is complete, one equivalent
5 of powdered sodium hydroxide is added, and the precipitated
desired polymer is removed, e.g. by filtration. The liquid
didodecylsulfide can be re-used in another polymerisation
reaction.

10 The chemical structure of the polymer reads, according to
formula I:

Q^1 = $C_{12}H_{25}$-; X^1 = absent; Y^1 = S-; Z = $(CH_2-C(H)(COONa))_{40-100}$-
; W = $-S-C_{12}H_{25}$
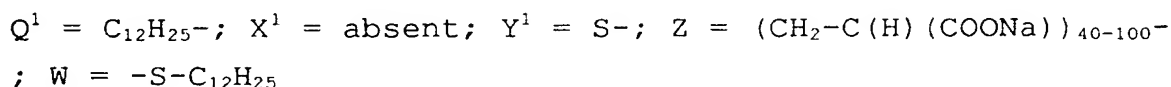
15

Example 5

Another way of preparing a sample with a significantly
higher proportion of double-endcapped dodecyl
20 poly(acrylate) as bridging agent for lamellar droplets is
by radical polymerisation of acrylic acid in dioxan solvent
using dodecanethiol as chain transfer agent and lauryl
peroxide initiator. One method to make this polymer is as
follows:
25

Acrylic acid (36 g, 0.5 mol), dodecanethiol (10.1g, 0.05
mol), dioxan (150 ml) where charged into a polymerisation
reactor. After purging the reactor with nitrogen for 30
minutes, Lauryl peroxide (1.2 g) was added and the
30 temperature was raised to 60°C. The polymerisation was
carried out for 10 hours. The polymer solution was cooled
to room temperature, and was neutralised with sodium

hydroxide solution (20 g NaOH). The solvent was removed using a rotary evaporator and can be re-used in another polymerisation reaction. The polymer was dissolved in water and precipitated into acetone. After purification by
5 two more dissolution/precipitation procedures, the polymer was characterised and was ready for use in liquid detergent products.

The weight average molecular weight (Mw), obtained by GPC
10 and converted to polyacrylate standards is 9,000-13,000. Hence, the chemical structure of the polymer reads, according to formula I:
$Q^1 = C_{11}H_{23}-$; X^1 = absent; $Y^1 = -COO-$; $Z = -(CH2-C(H)(COONa))_{90-135}-$;
15 $W = -S-C_{12}H_{25}$

Liquid Detergent examples

Examples 6

20

Component							Parts		
	6a	6b	6c	6d	6e	6f	6g	6h	6k
Na-LAS	28	28	28	28	28	28	28	28	28
Synperonic 7	12	12	12	12	12	12	12	12	12
Na-citrate	20	20	20	20	20	20	20	20	20
Deflocculating polymer (ref)	0.5	1.0	2.0				1.0	1.0	1.0
Deflocculating polymer (1)				0.5	1.0	2.0			
Deflocculating polymer (2)							0.25	0.5	1.0
Water	60	60	60	60	60	60	60	60	60
Physical properties									

40

Lamellar droplet deflocculation	good	good	good	good	good	good	good	good	good
Viscosity (mPa.s. at 21s-1)	30	70	90	100	70	230	60	100	1900

Deflocculating polymer (ref) = polymer A11 from EP-A-346,995

Deflocculating polymer (1) = polymer of Example 1 with a

5 MW = 7800

Deflocculating polymer (2) = polymer of Example 5 with a

MW = 9000 - 13000.

The results show that polymer (1) has similar

10 deflocculating ability as the reference polymer.
Differences are observed in effect on physical stability.
Polymer (1) is somewhat more efficient in obtaining
stability than the reference polymer. Furthermore, the
results suggest that polymer (2) works as a bridging and

15 viscosity enhancing polymer. The viscosity of example 6k
is much higher than the reference systems 6f and 6c.

Examples 7

20 Component	%w/w		
	7a	7b	7c
LAS-acid	16.5	16.5	16.5
Nonionic (Dobanol 25-7)	9	9	9
Oleic acid (Priolene 6907)	4.5	4.5	4.5
Zeolite	15	15	15
KOH, neutralisation of acid and pH to 8.5			
Citric Acid	8.2	8.2	8.2
Glycerol	2.0	2.0	2.0

Borax	1.5	1.5	1.5
Deflocculating polymer (ref)	1.0		
Deflocculating polymer (1)		0.5	1.0
Protease	0.38	0.38	0.38
Termamyl	0.07	0.07	0.07
Lipolase	0.2	0.2	0.2
Oily soil release polymer Aquaperle	0.5	0.5	0.5
Further minors	0.9	0.9	0.9
Water			to 100%
Physical properties:			
Lamellar droplet deflocculation	good	good	very good
Physical stability	border-line	OK	OK
Viscosity (mPa.s at 21s-1)	670	1250	1010

Deflocculating polymer (ref) = polymer All from EP 346,995
Deflocculating polymer (1)   = polymer of Example 1 with a
MW = 7800

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The results show that polymer (1) has better deflocculating ability as the reference polymer. The viscosities of the products are all in the range of good consumer acceptability for a pourable liquid.

10 The overall conclusion is that polymer (1) is more effective in obtaining the desired physical properties than the reference polymer.

Examples 8

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Component	%w/w		
	8a	8b	8c
LAS-acid	13.5	13.5	13.5
Nonionic (Dobanol 25-7)	4.5	4.5	4.5
Glycerol	4.37	4.37	4.37
Borax	2.79	2.79	2.79
STPP	18	18	18
KOH, neutralisation of acids to a pH of 7.5			
Deflocculating polymer (ref)	0.6		
Deflocculating polymer (1)		0.5	1.0
Protease	0.5	0.5	0.5
Lipolase	0.3	0.3	0.3
Oily soil release polymer Aquaperle	0.5	0.5	0.5
Antifoam	0.4	0.4	0.4
Perfume	0.4	0.4	0.4
Fluorescer	0.04	0.04	0.04
Water			to 100%

Physical properties:

	8a	8b	8c
Lamellar droplet deflocculation	border-line	good	good
Physical stability	border-line	good	good
Viscosity (mP.a.s at 21s-1)	630	510	1380

Deflocculating polymer (ref) = polymer A11 from EP 346,995

5 Deflocculating polymer (1) = polymer of Example 1 with a MW = 7800

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The results show that polymer (1) has better deflocculating
ability as the reference polymer. The overall conclusion
is that polymer (1) is more efficient in obtaining the
5 desired physical properties than the reference polymer.

In the light of this disclosure, modifications of the
described examples, as well as other Examples, all within
the scope of the present invention as defined by the
10 appended claims, will now become apparent to persons
skilled in the art.

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Claims

1.   An oligomer or polymer of formula (I)
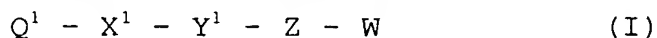
$$Q^1 - X^1 - Y^1 - Z - W \qquad \text{(I)}$$

wherein Q^1-represents a hydrophobic moiety, $-X^1-$ and $-Y^1-$ are independently each absent or represent a suitable linking group, $-Z-$ represents a hydrophilic chain; and $-W$ represents hydrogen or a group of formula $-Y^2-X^2-Q^2$, each of $-X^2, -Y^2$ and $-Q^2$ being independently selected from the values for X^1, Y^1 and Q^1 as hereinbefore defined.

2.   An oligomer or polymer according to claim 1, wherein Q^1- represents any optionally substituted C_5-C_{30} alkyl, C_5-C_{30} alkenyl or C_5-C_{30} aralkyl group or else is a hydrophobic monomer residue, preferably, a hydrophobically modified TEMPO moiety.

3.   An oligomer or polymer according to claim 1 or claim 2, wherein $-X^1-$ is absent or represents a group of formula $(-CH_2-)_n$ wherein n is 1 or 2 or X^1 is phenyl.

4.   An oligomer or polymer according to any preceding claim, wherein $-Y^1-$ is absent or represents a carbonyl group, an ester linkage, a hydroxy C_{1-15} alkyl group or a silyl group of formula $-SiR^1R^2$ where R^1 and R^2 independently represent $-CH_3$ or $-C_2H_5$.

5.   An oligomer or polymer according to any of claims 1-3, wherein $-W$ is other than hydrogen and $-Y^1-$ is selected from thia-, aza-, carboxy- (i.e. ester), carboxy aza-, phosphoryl-, phosphonyl- or phosphinyl- linkages.

6. An oligomer or polymer according to any preceding claim, wherein -Z- is selected from unsaturated acids and their corresponding salts, ethers, alcohols, aldehydes, ketones or esters, any of which have from 1 to 6 carbon atom; or -Z- is selected from cyclic monomer units which are unsaturated or comprise one or more groups capable of forming intermonomer linkage; or -Z- is selected from glycerol, polyalkylene oxide(s) and the unsaturated polyalcohol(s).

7. An oligomer or polymer according to any preceding claim, wherein -W represents hydrogen.

8. An oligomer or polymer according to any of claims 1-6, wherein -W represents a group of formula $-Y^2 -X^2 -Q^2$ wherein respectively, X^2, Y^2 and Q^2 are the same as X^1, Y^1 and Q^1.

9. An oligomer or polymer according to any preceding claim having a number average molecular weight of from 500 to 50,000.

10. A batch or sample of oligomer and/or polymer material comprising at least 50%, preferably at least 55%, more preferably at least 60%, still more preferably at least 65%, yet more preferably at least 70%, especially 75%, 80%, 85% or 95% by weight of an oligomer and/or polymer material according to any preceding claim.

11. A method of preparing an oligomer or polymer according to any preceding claim, the method comprising reacting a compound of formula (IV)

$$Q^1-X^1-Y^1-Y^2 \qquad\qquad (IV)$$

wherein Q^1 X^1 and Y^1 are as hereinbefore defined and Y^2 is a reactive hydrogen, or a free radical with a precursor material, in the presence of an initiator.

12. A method of preparing an oligomer or polymer according to any of claims 1-9, the method comprising reacting a compound of formula (V)

$$Q^1 - G - Q^1 \qquad\qquad (V)$$

wherein Q^1 is as hereinbefore defined with a precursor material as hereinbefore defined and Q^1-G-Q^1 is a molecule capable of cleavage to form a radical of formula Q^1-X^1-Y^1.

13. A liquid detergent composition comprising a dispersion of lamellar droplets in an aqueous continuous phase, the composition further comprising an oligomer or polymer of formula (I), according to any of claims 1-9, or a sample or batch of oligomer or polymer material according to claim 10.

14. A composition according to claim 13, the composition comprising both at least one oligomer or polymer according to claim 7 and at least one oligomer or polymer according to any of claims 1-6, wherein -W represents a group of formula $-Y^2$ $-X^2$ $-Q^2$ wherein X^2, Y^2 and Q^2 are as defined in claim 1.

15. A composition according to claim 13 or claim 14, which composition comprises from 0.01 to 5% by weight in total of

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the one or more oligomers or polymers according to any of
claims 1 to 9 of a sample or batch of oligomer and/or
polymer material according to claim 10.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6   C11D3/37   C08F220/04

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6   C11D   C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	EP 0 623 670 A (ALBRIGHT & WILSON LTD.) 9 November 1994 cited in the application ---	
A	US 5 489 397 A (P. BAINBRIDGE) 6 February 1996 cited in the application ---	
A	WO 96 02622 A (BASF CORP.) 1 February 1996 -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 September 1998	22/09/1998

Name and mailing address of the ISA	Authorized officer
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